H abstraction dynamics by crossed-beam velocity map imaging: $Cl + CH_3OH \rightarrow CH_2OH + HCl$

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Abstract

The crossed-beam reaction of ground state Cl ($^2P_{3/2}$) atoms with CH_3OH have been studied using the technique of velocity map imaging (VELMI). The hydroxymethyl (CH_2OH) radical was detected via single-photon ionization using 157 nm laser light. The full double-differential cross-sections were obtained at a collision energy of 8.7 kcal/mol. The angular distribution was predominantly in the sideways-backward direction with respect to the incoming alcohol beam, suggesting direct abstraction dynamics. The average translational energy release was 6.1 kcal/mol, out of 15.1 kcal/mol available. The technique of vacuum ultraviolet one-photon ionization in conjunction with VELMI promises to be useful for studying the reaction dynamics for many polyatomic systems. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Abstraction reactions of hydrogen atoms from hydrocarbons are of great importance in combustion. There has been an explosion of studies with the advent of laser technology and development of new techniques in studying such processes, particularly for the reactions of O and Cl with saturated hydrocarbons [1]. Alcohols have become important as alternative fuels in recent years, and their combustion dynamics clearly merits more detailed investigation. There have been a few kinetic studies focussing on H abstraction from alcohols by O, Cl, and OH, but these have only generated rate-information; there have been no experimental dynamics studies performed on the bimolecular reactions of alcohols.

We have undertaken a series of experiments to study the dynamics of H atom abstraction from alcohols by Cl atoms using crossed molecular beams in conjunction with velocity map imaging. Ion imaging is a multiplexing method which provides simultaneous detection of all recoil velocities, both speed and angle, for the detected product [2]. Furthermore, the images may be directly deconvoluted to yield the velocity–flux contour maps which summarize the dynamics. This deconvolution does not require the simplifying assumption of uncoupled translational energy and angular distributions usually employed in analyzing reactive scattering experiments, so the imaging experiments thus directly reveal the genuine double-differential cross-sections ($d^2\sigma/dE_T(\cos\theta)$). Another advantage of the imaging technique, particularly in the present studies, is the absence of any kinematic limitations on the reactions. Products scattering much faster or much slower than the beams themselves may be as easily detected.

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In the past, the ion imaging technique has suffered from limited velocity and angular resolution, largely determined by the dimensions of the interaction region relative to the detector, and by blurring from lensing effects associated with the grids. A recent advance by Eppink and Parker [3] involves simply replacing the conventional grids of the Wiley–McLaren time-of-flight (TOF) spectrometer with open electrostatic lenses and adjusting the potentials to achieve momentum focusing. Under these conditions, termed 'velocity map imaging' (VELMI), all products with the same initial velocity vector in the plane parallel to the detector are focused to the same point, irrespective of their initial distance from the ion lens axis. Very recently we performed the first experiment utilizing VELMI to study the reaction dynamics of the $O(^1D) + D_2 \rightarrow OD + D$ system [4]. Despite the advantages of the crossed-beam imaging technique, there have been relatively few such studies. Almost all have been performed using $1 + 1$ resonant multiphoton ionization (REMPI) [4–6]. While there are many more species that could be detected using $2 + 1$ REMPI, sensitivity issues (small interaction volume owing to the tight laser focus, low cross-sections) have precluded their use except in a few recent cases of inelastic scattering [7]. Recently, groups at Cornell [8–10] and Berkeley have used vacuum ultraviolet (VUV) radiation to perform one-photon photoionization detection of polyatomic radical fragments from bimolecular reactions. The Berkeley group used tunable synchrotron radiation with a 'traditional' crossed-beam configuration to detect hydrocarbon radicals formed in bimolecular reactions of Cl with propane [1] and *n*-pentane [11]. The Cornell group has pioneered the use of 157 nm radiation generated by the F_2 excimer laser to photoionize products formed in metal–hydrocarbon bimolecular reactions [8]. We adapted the latter probe to our crossed-beam velocity map imaging experiment. Here we present results for the $Cl + CH_3OH \rightarrow CH_2OH + HCl$ reaction, where the hydroxymethyl radical was detected by single-photon ionization.

2. Experimental

The crossed molecular beams apparatus (Fig. 1) has been described in detail in recent publications
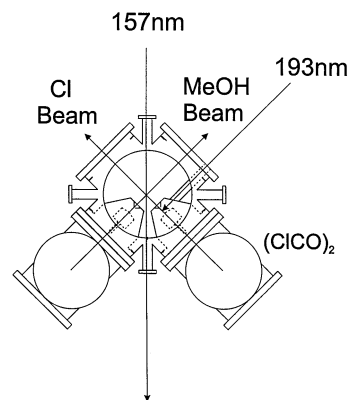

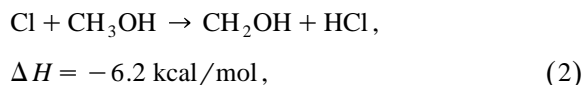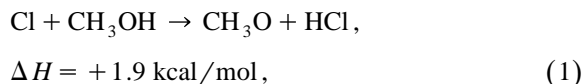Fig. 1. Schematic of crossed-beam VELMI apparatus.

from our group [4,12]. The Cl beam was generated by photodissociation of oxalyl chloride $[(ClCO)_2]$ seeded in He, using the 193 nm output of a ArF excimer laser (60 mJ, 10 Hz Lambda Physik) at the nozzle of a Proch-Trickl piezoelectric pulsed valve [13]. The molecular beam of $(ClCO)_2$ was generated by passing helium through a bubbler containing oxalyl chloride, held at 6°C. The photodissociation dynamics of oxalyl chloride have recently been examined in our laboratory and photodissociation at 193 nm yields predominantly Cl, Cl^* and CO [14]. The Cl atom beam velocity and spread was monitored using $(2 + 1)$ REMPI of $Cl(^2P_{3/2})$ via the $4p\,^2D_{3/2} \leftarrow \leftarrow 3p\,^2P_{3/2}$ transition at 235.336 nm [15]. The UV photodissociation of oxalyl chloride also generates the spin-orbit excited $Cl^*(^2P_{1/2})$ which was monitored using the $4p\,^2P_{1/2} \leftarrow \leftarrow 3p\,^2P_{1/2}$ transition at 235.205 nm. The Cl^*/Cl ratio was 1:50 and 1:62 for oxalyl chloride seeding in He and Ar, respectively, or better than 98% ground state Cl, using relative linestrengths for the transitions as discussed in Ref. [12]. We believe the efficient quenching is likely induced by many Cl–CO collisions. Methanol seeded 2% in He was expanded through another Proch-Trickl pulsed valve, collimated by a single skimmer and the beams were allowed to interact on the axis of the velocity-focusing TOF mass spectrometer.

Light from a 157 nm excimer laser (1–2 mJ, 10 Hz, Lambda-Physik) was focussed loosely into the interaction region of the two crossed beams and used to ionize the hydroxymethyl radical reaction product.

The CH_2OH^+ ion was accelerated toward a 80 mm diameter dual microchannel plate (MCP) detector coupled to a fast phosphor screen (P-47) and imaged on a fast-scan charge-coupled device camera with integrating video recorder (Data Design AC-101 M). Camera threshold and gain were adjusted in conjunction with a binary video look-up table to perform integration of single-ion hits on the MCP free of video noise. The recorded image is actually a two-dimensional (2-D) projection of the nascent three-dimensional (3-D) velocity distribution, and established tomographic techniques [2] were used to reconstruct the 3-D distribution. The velocity dependence of the detection efficiency [4] was minimized by timing the probe very soon after the arrival of the Cl beam to minimize accumulation of slow products in the interaction region, and by symmetrizing the image using only that half that has the faster lab velocity. Typical accumulation time for a single-collision energy was ~ 30 min.

3. Results and discussion

The reaction of methanol with chlorine atoms has been studied in a number of laboratories using traditional kinetic methods, summarized in Ref. [16]. The rate of reaction is moderately fast, $(5.3–6.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, with no appreciable barrier. The reaction of Cl with methanol can proceed via two channels:

$$Cl + CH_3OH \rightarrow CH_3O + HCl,$$

$$\Delta H = +1.9 \text{ kcal/mol}, \tag{1}$$

$$Cl + CH_3OH \rightarrow CH_2OH + HCl,$$

$$\Delta H = -6.2 \text{ kcal/mol}, \tag{2}$$

channel (1) and (2) forming the methoxy and hydroxymethyl radicals respectively. The branching ratio for the latter channel has been found to be experimentally close to unity, 0.95 [16]. The ionization potential (IP) for CH_3O is 10.72 eV [17] (and the CH_3O^+ ion is unstable [18]) so that we will not be sensitive to this channel. However, the IP for CH_2OH is 7.56 eV [19], so that single-photon ionization using the 157 nm laser light (7.9 eV) will readily probe this product from channel (2) above.

Fig. 2 shows a data image of the product formed at mass 31, CH_2OH^+, from the reaction of Cl with methanol probed with 157 nm laser light. The relative velocity vector is vertical in the plane of the figure, and the Newton diagram for the scattering process has been superimposed on the image. There is substantial photodissociation of methanol at 157 nm which also produces CH_2OH. This shows up as the ring centered at the methanol beam. As is immediately apparent from the image, this creates a problem in extracting information for forward scattering relative to the incoming alcohol beam. We have subtracted an image recorded with the 193 nm laser off from one recorded with the laser on to remove the photodissociation contribution from the reactive scattering image. Unfortunately, the intense photochemical signal creates substantial noise and corresponding uncertainty in the reactive flux formed between 0 and 46° as indicated in the image; we do not display the results of the angular distribution for the unreliable region. However, we can extract the differential cross-section reliably from the rest of the image. At a collision energy E_{coll} of 8.7 kcal/mol, there is 15.5 kcal/mol energy available to be distributed into translation and the internal energy of the products. The outer ring in Fig. 2 shows the
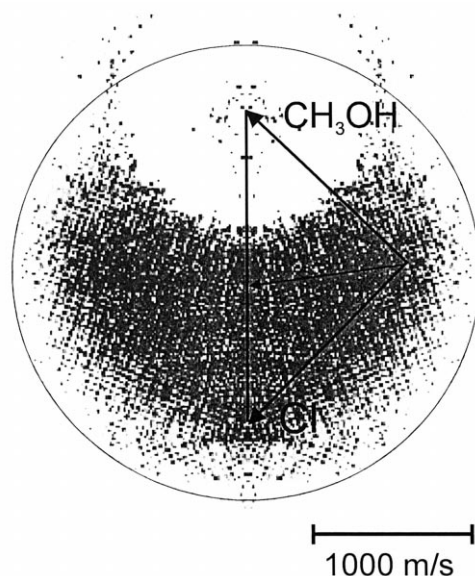

Fig. 2. Data image for hydroxymethyl radical product of crossed-beam $Cl + CH_3OH$ reaction at 8.7 kcal/mol collision energy.
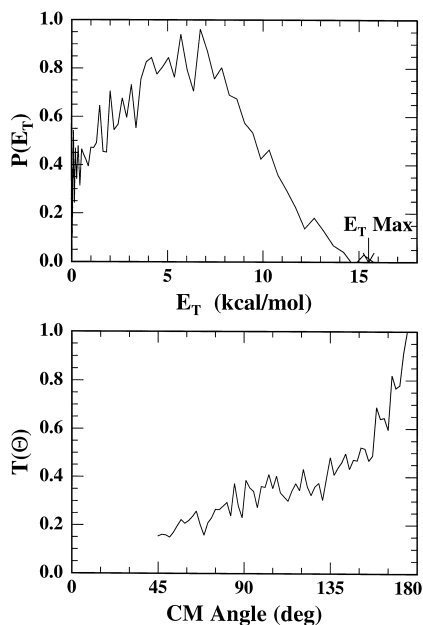
Fig. 3. Translational energy (top) and angular distribution (bottom) for hydroxymethyl radical from image data in Fig. 2. Forward scattering (0°) corresponds to the methanol beam direction.

maximum recoil speed allowed for the CH_2OH radical; there is reactive flux virtually to the limit of available energy in the sideways and backward direction. The cylindrical symmetry of the experiment justifies the use of the inverse Abel transform method to reconstruct the full 3-D distributions, so that this analysis is, in effect, a direct inversion of the experimental data. The c.m. angular distribution extracted from the images is shown in Fig. 3. There is substantial sideways scattering – the ratio of sideways (90°–120°) to backward (150°–180°) is 1.75. The translation energy distribution obtained from the reconstructed data is also shown in Fig. 3. The average translational energy released is 6.1 kcal/mol, or 39% of the available energy.

The enhanced sideways-backscattered distribution seen in our experiment indicates direct reaction dynamics. Jodkowski et al. [20] have performed ab-initio calculations at different levels of theory and using several basis sets to characterize stationary points on the potential surface for the reaction of Cl with CH_3OH. They found several minima, including one in the entrance channel corresponding to Cl attaching to the O atom and another in the exit channel

resembling a hydrogen-bonded complex between HCl and CH_2OH, with the latter representing the minimum point on the surface, 10.0 kcal/mol below the reactants. The presence of these minima led them to suggest that reaction occurs via formation of an intermediate complex similar to the $CH_3OH + F$ reaction [21]. No exit-barrier was found in their calculation for the $CH_2OH + HCl$ channel. However, they generated only a few stationary points on the surface and did not explicitly consider the reaction path. Our results clearly show the importance of a direct reaction mechanism, at least at our 8.7 kcal/mol collision energy. Further calculations would be very useful to probe the mechanism of these reactions in greater detail.

4. Conclusions

These results demonstrate the power of VELMI combined with single-photon VUV ionization. Work is currently underway in our laboratory on reactions with other alcohols, and analogous reactions of O and OH should be quite feasible. With judicious choice of chemical system and probe light sources, the detailed and systematic investigation of the dynamics for many polyatomic reactions promises to become routine.

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